

is a better approximation for ψ near the cell boundary than is the first term of equation (15). Series (24) involves quite a number of terms, but the magnitude of each term can be computed fairly accurately by the use of only a few F 's.

This observation illustrates the differences and the relative advantages of the augmented-plane-wave method of computing ψ and the method discussed in the present paper. The quantities inside the braces in equation (24) can be considered as the unknown coefficients (the B 's of equation [3]), and equation (5) can be integrated to produce a set of simultaneous equations⁴ for the B 's which can be solved to find k^2 and ψ . Equation (5), however, involves the value and normal gradient of ψ at the surface of the sphere, where it can be represented by fewer terms in the expansion form (1) than by form (3). Therefore, the secular equation using the F 's involves fewer terms than does that using the B 's. Once the secular equation is solved, however, and the F 's are obtained, to compute ψ near the cell boundary it is often better to use series (24) than series (15).

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DETERMINATION OF CRYSTAL STRUCTURES BY MEANS OF ANOMALOUSLY SCATTERED X-RAYS

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A new method of analysis of noncentrosymmetric crystals has been reported from this laboratory by Okaya, Saito, and Pepinsky.¹ The method involves use of anomalous scattering of X-rays. When dispersion occurs, the atomic scattering factor, f_j , becomes complex:

$$f_j = (f_0)_j + \Delta f_j' + i f_j'' = f_j' + i f_j''. \quad (1)$$

Here $(f_0)_j$ is the scattering factor at infinite wave length, $\Delta f_j'$ is the real part of the change in this factor near an absorption edge, and f_j'' is the imaginary part on the short-wave-length side of the absorption edge. We found it very useful to examine the value of the square of the amplitude of the crystal structure factor, $|F_{hki}|^2 = F_{hki} \cdot F_{hki}^*$, and the Fourier series involving these quantities as coefficients, when anomalous scatterers are present in the structure; we demonstrated that

$$|F_{hkl}|^2 = \sum_{j,k} (f_j' f_k' + f_j'' f_k'') \cos 2\pi[h(x_j - x_k) + k(y_j - y_k) + l(z_j - z_k)] + \sum_{j,k} (f_j' f_k'' - f_j'' f_k') \sin 2\pi[h(x_j - x_k) + k(y_j - y_k) + l(z_j - z_k)], \quad (2)$$

and

$$P_{\text{anom. scatt.}}(u, v, w) = \sum_{hkl}^{\infty} |F_{hkl}|^2 \cdot \exp[-2\pi i(hu + kv + lw)] \\ = P_c(u, v, w) - iP_s(u, v, w), \quad (3)$$

where

$$P_c(u, v, w) = \sum_{hkl}^{\infty} |F_{hkl}|^2 \cos 2\pi(hu + kv + lw) \quad (4)$$

and

$$P_s(u, v, w) = \sum_{hkl}^{\infty} |F_{hkl}|^2 \sin 2\pi(hu + kv + lw). \quad (5)$$

It is readily shown that $P_{\text{anom. scatt.}}(u, v, w)$ is the convolution of the (now complex) electron-density function

$$\rho(x, y, z) = \sum_{hkl}^{\infty} F_{hkl} \cdot \exp[-2\pi i(hx + ky + lz)] \quad (6)$$

with the complex conjugate function

$$\rho^*(x, y, z) = \sum_{hkl}^{\infty} F_{hkl}^* \cdot \exp[2\pi i(hx + ky + lz)]. \quad (7)$$

It is then apparent that $P_c(u, v, w)$ has peaks of height corresponding to form factors $f_j' f_k' + f_j'' f_k''$ at the points $\pm(u, v, w) = \pm(x_j - x_k, y_j - y_k, z_j - z_k)$; and $P_s(u, v, w)$ has peaks of height corresponding to form factors $f_j' f_k'' - f_j'' f_k'$ at points $(u, v, w) = (x_j - x_k, y_j - y_k, z_j - z_k)$ and peaks of height corresponding to $-(f_j' f_k'' - f_j'' f_k')$ at points $(-u, -v, -w) = (x_k - x_j, y_k - y_j, z_k - z_j)$.

Our earlier communication¹ was concerned with a preliminary account of the usefulness of the function $P_s(u, v, w)$. This function indicates vectors between unlike anomalous scatterers and between anomalous and nonanomalous scatterers, and it reveals the *sense* of the vectors between these atoms. One would ordinarily not expect to have more than one kind of anomalously scattering element per cell, for a properly selected exciting radiation. Usually, then, if M atoms, of one species only, scatter anomalously, so that $f_j'' = 0$ unless $j = m_1, m_2, \dots, m_M$, then $P_s(u, v, w)$ has peaks of height corresponding to the form factors $f_j f_m''$ at $[(x_j - x_m), (y_j - y_m), (z_j - z_m)]$ and corresponding to $-f_j f_m''$ at $[(x_m - x_j), (y_m - y_j), (z_m - z_j)]$. The sense of the noncentric distribution of nonanomalous scatterers about an anomalous scatterer, and hence the absolute configuration, is thus established. Furthermore, the number of peaks is always very much less than the number in a normal Patterson map. If there are N atoms per cell, and M of these are anomalous

scatterers of one type only, P_s contains $M(N - M)$ positive peaks and an equal number of negative peaks.

With M anomalous scatterers of only one species per cell (the usual case), we set $f_k' = f_k$, $f_k'' = 0$ for the normal scatterers, and we can write, from equation (2),

$$|F_{hkl}|^2 - |F_{\bar{h}\bar{k}\bar{l}}|^2 = 2Mf_j'' \sum_k f_k \sin 2\pi[h(x_k - x_j) + k(y_k - y_j) + l(z_k - z_j)]. \quad (8)$$

Thus the difference between intensities I_{hkl} and $I_{\bar{h}\bar{k}\bar{l}}$ depends on the imaginary component only of the anomalous scatterer and on the atomic structure factors and dispositions of the normally scattering atoms around each anomalous scatterer. The larger the component f_j'' , the more significant is the difference $I_{hkl} - I_{\bar{h}\bar{k}\bar{l}}$ and the more useful is the function $P_s(u, v, w)$. The practical limitation to the use of the method arises from the limits of accuracy within which the values of $|F_{hkl}|^2$ and $|F_{\bar{h}\bar{k}\bar{l}}|^2$ can be measured.

The new function has been applied to the structure of $2[d\text{-Co(en)}_3]\text{Cl}_3 \cdot \text{NaCl} \cdot 6\text{H}_2\text{O}$ (en = ethylenediamine), and the structure was directly determined.² The method has also been successfully applied to cobaltous aspartate trihydrate³ and to the structure of $[d\text{-Co(en)}_3]\text{Br}(d\text{-tartrate}) \cdot 5\text{H}_2\text{O}$.⁴ The latter structure is in space group $P1$, and there is but one molecule per cell; hence the method is particularly applicable to it.

Our first use of the new anomalous-scatterer method had depended upon dispersion from K electrons in elements in the range from vanadium (23) to ruthenium (44). The differences between $|F_{hkl}|^2$ and $|F_{\bar{h}\bar{k}\bar{l}}|^2$ can be expected to be significant if the value of f_j'' is above 3.0. An examination of values of f_k'' values for these elements, as presented in the treatises of Compton and Allison⁵ and James,⁶ shows that values between 3.0 and 3.5 can be achieved if the incident wave length is $K\alpha$ radiation from a target or from a fluorescence-excited source of an element from 2 to 3 atomic numbers higher than the anomalously scattering atom. $L\alpha$ radiation is a preferable exciting wave length for certain elements (W $L\alpha$ to excite Ni K electrons, Ir $L\alpha$ for Cu, Au $L\alpha$ for Zn, Th $L\alpha$ for As or Se, U $L\alpha$ for Br). It should be noted that the form factor for these anomalously scattering K electrons is essentially isotropic, because the electrons involved are so close to the nuclei of the atoms concerned. Hence the value of $(f_K)_j''$ is maintained even at high scattering angles, and the peaks in $P_s(u, v, w)$ have essentially the shape of the electron-density peaks for the nonanomalous scatterers. This excepts, of course, the effects of thermal oscillation, which may be reduced by means of a suitable temperature factor. The peaks may all be sharpened by the usual method of division of $|F_{hkl}|$ by an average atomic structure factor for the nonanomalous scatterers. The influence of $(f_K)_j''$ is large, therefore, when the structure is comprised of light atoms (carbons, nitrogens, oxygens, etc., whose atomic structure factors fall off fairly rapidly with increasing scattering angle) about the anomalous scatterer.

X-ray tubes are commercially available for excitation of anomalous scattering by K electrons in V, Cr, Mn, Fe, Co, Ni, Rb, Sr, and Y. Other atoms must be excited by special targets in demountable tubes or by the use of fluorescent incident radiation. Excited fluorescent radiation should be reduced by the use of a suitable absorbing filter. A preferable technique utilizes a direct photon-counting detector, with a monochromatizing crystal set up in front of, and mounted integrally with,

the detector, in such a way that only the incident wave length passes through slits into the detector. A fluorescent source can then be used *without* monochromatizing *before* the crystal under study; and, of course, fluorescent radiation is prevented from reaching the detector. Alternatively, a suitable filter can be placed over the detector window.

Dauben and Templeton⁷ have recently computed $\Delta f_j'$ and f_j'' values for both K and L electrons in elements from Ca (20) to the end of the periodic table, and for Cr, Cu, and Mo $K\alpha$ radiation. The calculations are based on observations of Eisenlohr and Müller⁸ and Parratt and Hempstead.⁹ We also have obtained extrapolated values of f_j'' for $K\alpha$ radiation from Mn, Fe, Ce, and Ni targets.¹⁰ These values of f_j'' are very striking. For Cr $K\alpha$ radiation, for example, f_j'' rises from 2.7 for Br (35) to 14 for I (53). The maximum value of f_j'' is about 14 for Cs (55) excited by Mn $K\alpha$, about 13 for Ba (56) excited by Fe $K\alpha$, about 12 for La (57) excited by Co $K\alpha$, and the same for Ce (58) excited by Ni $K\alpha$. The f_j'' value is 7.2 for I (53) excited by Cu $K\alpha$ and 8.3 for Cs (55) and 8.9 for Ba (56) similarly excited. For elements heavier than the rare earths and up to Rn (86), Mo $K\alpha$ radiation is an excellent exciting radiation; f_j'' increases from 7.4 for Ta (73) to 12 for Bi (83), with Mo $K\alpha$. Rh or Ag targets would also be useful in this range. With exciting wave lengths between Cr $K\alpha$ and Cu $K\alpha$, the dispersion effects in this range of elements are also very significant. For Pb (82), for example, f_{Pb}'' is 16 for Cr $K\alpha$ and 9 for Cu $K\alpha$. It is generally possible to include one or another of atoms such as Br, Rb, Sr, Pd, Ag, Cd, Sn, Sb, Te, I, Cs, or Ba in an organic crystal; and others of the series can be incorporated by the "crystal-engineering" methods.¹¹ The difference between $|F_{hkl}|^2$ and $|F_{\bar{h}\bar{k}\bar{l}}|^2$ for crystals containing such elements, and for properly selected incident wave lengths, should be very large. It has been shown¹² that the values of $\Delta f_j'$ and f_j'' are effectively independent of scattering angle, just as in the case for the K electrons.

Differences between $|F_{hkl}|^2$ and $|F_{\bar{h}\bar{k}\bar{l}}|^2$ should be clearly visible in the $(0kl)$ intensities of tetragonal (ferroelectric) $PbTiO_3$, for example, when a single-domain crystal is radiated with Mo $K\alpha$ X-rays. Unfortunately, the specimen used in a recent X-ray analysis in this laboratory¹³ was multi-domain, and (hkl) and $(\bar{h}\bar{k}\bar{l})$ reflections were superposed in the scattering patterns. A P_s map utilizing single-domain crystal data should reveal the structure of this ferroelectric without recourse to neutron-scattering information.¹³ The value of f_{Pb}'' is about 11, there is one Pb per cell, and neither Ti nor O contributes measurably to the anomalous scattering. The technique is presently being applied to the structure of tetragonal PbO , since untwinned crystals of this compound are available.

Absorption effects will be very pronounced for measurements of crystals containing elements of relatively high atomic numbers when wave lengths from Cr $K\alpha$ to Cu $K\alpha$ are used. One must then employ very small crystals and make absorption corrections for these. Such corrections are likely to be very difficult to make unless the crystal cross-sections are accurately circular. The Airbrasive lathe cutting method¹⁴ is not suitable for cutting crystals below 0.1 mm. in diameter; and, indeed, no method has been introduced heretofore which will permit accurate cutting of cylinders with diameters below 100 μ . A new method, which serves excellently for crystal-shaping under a microscope, has been devised and reported separately.¹⁵ This utilizes a high-frequency magnetostriuctive transducer, to which

a microcutting tool is attached, and the entire cutting assembly is mounted on a micromanipulator.

The present method differs from that utilized so excellently by Bijvoet *et al.*¹⁶ and Saito *et al.*¹⁷ The earlier methods require that the crystal structure first be solved by standard methods; then certain pairs of factors $|F_{hkl}|$ and $|F_{\bar{h}\bar{k}\bar{l}}|$ are examined, to permit a choice between right- and left-handed configurations. Our procedure is to utilize *all* pairs of values $|F_{hkl}|^2$ and $|F_{\bar{h}\bar{k}\bar{l}}|^2$ in the P_s function and to obtain directly the distribution of non-centrally-related atoms around the anomalous scatterers. Once this distribution is determined, the complete structure may be found by image-seeking methods¹⁸ or by various standard procedures. In effect, the earlier methods used only half the available X-ray scattering data at the outset of the analyses and then applied differences between $|F_{hkl}|$ and $|F_{\bar{h}\bar{k}\bar{l}}|$, after the structure was determined *except* for choice of hand, to deduce the absolute configuration. *Our method utilizes all the information at the outset, and very significant assistance is provided in solution of the phase problem.* Indeed, the method places the solution of noncentric crystals on a new basis; when an anomalously scattering element is present in a moderately complex noncentric structure, the X-ray analysis should now be fairly straightforward. Whereas one formerly sought to analyze noncentric crystals via centrosymmetric projections, at the outset (and difficulties often arose because of overlapping in these projections), the new method renders noncentric distributions containing an anomalous scatterer easier to analyze than centric distributions.

Two matters should be mentioned at this point. *The interpretation of the P_s function is unambiguous in space group $P1$.* In other noncentric space groups it is necessary to remove ambiguities introduced by rotational and/or translational symmetries. *Image-seeking designed to unravel these effects should be accomplished directly on the P_s function itself, but utilizing information concerning the positions of anomalous scatterers as available from the full Patterson function P_c alone or the $P - P_c$ function discussed below.* It has been found possible to compute Buerger's image-seeking minimum function¹⁸ in three dimensions directly on X-RAC and S-FAC; details of such image-seeking in the P_s , P_c , or $P - P_c$ functions have been reported elsewhere.¹⁹

The second matter concerns the usefulness of direct examination of (hkl) and $(\bar{h}\bar{k}\bar{l})$ reflections, when anomalous scatterers are present in a structure, to establish whether or not the structure is centrosymmetric. This is an obvious application, but it has been overlooked by some investigators. Proper choice of wave length of the primary X-ray beam will maximize this effect.

It is useful to examine the function $P_c(u, v, w)$ (eq. [4]), which we have shown to contain peaks of height corresponding to form factors $f_j'f_k' + f_j''f_k''$ at the points $\pm(u, v, w)$, when anomalous scatterers are present. The $f_j''f_k''$ term will vanish unless both j and k refer to anomalous scatterers, and again one can usually choose an incident wave length such that there will be only one type of anomalous scatterer per cell. The P_c function will prove very useful when it is compared with a usual Patterson function *without* anomalous scattering. Values of $\Delta f'$ for K-electron dispersion can be found in Compton and Allison⁵ and in James,⁶ and Dauben and Templeton⁷ provide some $\Delta f'$ values for L-electron dispersion. The $\Delta f'$ value can be very significant indeed; it is about 12, for example, for Cr $K\alpha$ radiation

scattered by Cs or Ba,⁷ and 3 for Cu $K\alpha$ scattered by Ni. It is well known that the graph of $\Delta f'$ versus exciting wave lengths has very sharp peaks, in contrast to the variation of f'' versus λ ; $\Delta f'$ has significant (negative) values when the exciting wave length is very close to the absorption edge of the anomalous scatterer (cf. Hönl²⁰). f_j'' has values only on the short-wave-length side of the absorption edge.

Variations in $\Delta f'$ and f'' with wave length can, of course, be applied in a technique similar to the isomorphous replacement method.²¹ In contrast to the usual cases of isomorphous atomic replacement—e.g., Cl replaced by Br—the isomorphism here is *precise*. By proper choice of exciting wave lengths and anomalous scatterers, it is even possible to achieve the equivalence of precise multiple isomorphism (e.g., I or Cs atoms scattering Cr $K\alpha$, Cu $K\alpha$, and Mo $K\alpha$ radiation).

Let us consider the function $P(u, v, w) - P_c(u, v, w)$, where dispersion is not involved in the coefficients for $P(u, v, w)$ but is involved in $P_c(u, v, w)$. Peaks in this difference function will correspond to scattering factors equal to

$$[(f_0)_j - \Delta f_j'][(f_0)_k - \Delta f_k'] + f_j'' f_k'' - (f_0)_j (f_0)_k = \Delta f_j' \cdot \Delta f_k' + f_j'' \cdot f_k'' - (f_0)_j \cdot \Delta f_k' - (f_0)_k \cdot \Delta f_j'. \quad (9)$$

If the j th atom scatters anomalously but the k th does not, the peak height will be determined by $(f_0)_k \cdot \Delta f_j'$. Peaks representing interactions of like species of anomalous scatterers will be of height determined by

$$(\Delta f_j')^2 + (f_j'')^2 - 2(f_0)_j \Delta f_j'.$$

(It is to be remembered that the value of $\Delta f_j'$ is negative in the region of anomalous dispersion.) Peaks representing interactions between nonanomalous scatterers will, of course, not appear in the difference function. If there are M (similar) anomalous scatterers $j = 1, 2, \dots, m, \dots, M$ per cell, and $N - M$ nonanomalous scatterers, there are $M(N - M)$ peaks of height determined by $f_k \cdot \Delta f_m'$, representing the distribution of nonanomalous scatterers about the anomalous scatterers, and there are $M(M - 1)$ peaks of height determined by $[(\Delta f_m')^2 + (f_m'')^2 + 2|(f_0)_m \cdot \Delta f_m'|]$. This situation is to be compared with that for the normal Patterson P or the P_c function, where there are $N(N - 1)/2$ peaks not related by the symmetry center.

It should be emphasized that the function $P - P_c$ applies to both centrosymmetric and noncentrosymmetric crystals or crystal projections, while P_s serves only for noncentric density distributions. The function $P - P_c$ is centrosymmetric always and contains peaks representing distances between like anomalous scatterers, when more than one of these is present in each cell, and also peaks for interactions between anomalous and normal scatterers. The function P_s is noncentric, contains interactions between anomalous and normal scatterers only, if only one type of the former is present per cell, and directly gives the absolute configuration of normal scatterers about the anomalous scatterers.

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SOUND TRANSMISSION IN THE TURTLE'S EAR*

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Though a number of writers have expressed doubts about the hearing abilities of the turtle, and some have gone so far as to regard its ear as degenerate and largely or even wholly unresponsive to sounds, it is easy to show by both behavioral and electrophysiological methods that an auditory function is present. We have recently recorded the electrical potentials produced in the inner ear in response to sounds for a number of turtle species and have made detailed measurements on three of these: the wood turtle, *Clemmys insculpta*; the painted turtle, *Chrysemys picta picta*; and the "Cumberland" turtle, *Pseudemys scripta*.¹ These results show an excellent auditory function within certain limits of frequency and intensity. For tones up to 700 cycles, the sensitivity, when expressed as the sound pressure required to produce some small value of inner-ear potential, is of the same order of magnitude as that similarly measured in the mammals, such as the cat, for the same